consider the solvent function of the solvent in such a reaction (ignoring its reactant function). Obviously if the solubility of the derived lignins is a limiting factor in the reaction, high yields will be obtained only with the better lignin solvents.[6] A perusal of the literature suggest this to be the case. Fuchs reports nearly complete lignin removal with the excellent solvents phenol and "methoxyglycol,"[7] while methanol[8] and ethanol[9] give only poor yields from the same wood. Increasing the quantity of ethanol increases the yield of ethanol lignin,[10] as would be expected.

Experiments outlined in Fig. 1 are believed to separate largely the solvent and reactant effects of the solvent in a typical reaction. One-gram samples of dry alcohol- and ether-extracted spruce wood meal (100 mesh) were treated in sealed glass tubes at 60–62° with 15 ml. of solvent mixtures varying from pure dioxane to pure methanol,[11] all containing 2% hydrogen chloride. Runs were made for 48 and 64 hours. By means of a Beckman quartz spectrophotometer, the optical density of the various solutions (diluted 625 times with pure dioxane) at wave lengths 275 and 280 mμ was determined and was used as a semiquantitative measure of lignin removal.[12] With pure dioxane, the lignin removal was small, since functional groups suitable for reaction with the lignin are present only fortuitously in the solvent.[13] On adding methanol, the yield of lignin increased to a maximum, which was greater than the sum of that formed in either pure solvent, and then decreased as the poor solvent power of the methanol limited the solubility of the product.

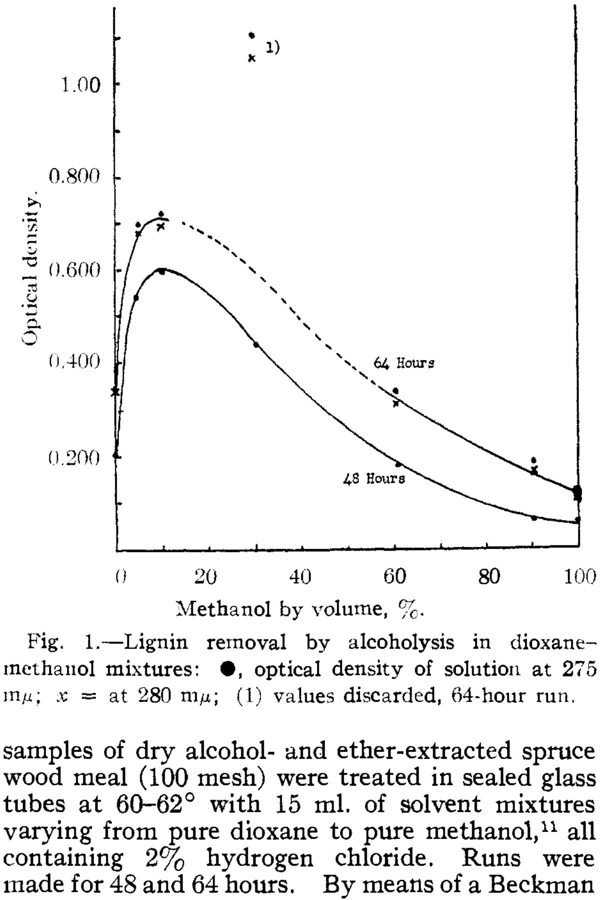


Fig. 1.—Lignin removal by alcoholysis in dioxane-methanol mixtures: ●, optical density of solution at 275 mμ; x = at 280 mμ; (1) values discarded, 64-hour run.

This observation is of obvious general application to lignin isolation procedures and indicates that the low reported yields of lignin alcoholysis products are mainly the result of the slight solubility of the products in the solvent rather than solely the result of polymerization reactions, as might be inferred from earlier work.[10] It does not constitute proof of the original assumptions or of the absence of such polymerization reactions.

Acknowledgment.—The author is indebted to Mrs. M. Granath for the determinations of optical density reported herein.

---

[6] Fragments of larger molecular weight will also dissolve in quantity in the better solvents.

[7] W. Fuchs, THIS JOURNAL, **58**, 675 (1936).

[8] M. Phillips in Wise's "Wood Chemistry," Reinhold Publishing Corp., New York, N. Y., 1944, p. 289.

[9] L. Brickman, J. J. Pyle, J. L. McCarthy and H. Hibbert, THIS JOURNAL, **61**, 868 (1939).

[10] W. B. Hewson, J. L. McCarthy and H. Hibbert, *ibid.*, **63**, 3041 (1941).

[11] The methanol was a commercial anhydrous grade, the dioxane a purified grade refluxed with hydrochloric acid, dried over sodium hydroxide, and distilled from sodium; *cf.* Fieser's "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., 1941, p. 368. Customary but not extreme precautions were taken to ensure the absence of alcohols and water. The nature of the substrate and the complexity of the reaction tend to make absolute precision difficult to obtain and at present perhaps not too significant.

[12] This method of analysis for lignin is arbitrary and subject to some obvious errors, as are all others. In view of the similarity of the systems used in these experiments, semiquantitative validity appears assured.

[13] Freudenberg claims no removal of lignin in the absence of alcohols, according to F. Brauns in Ott's "Cellulose and Cellulose Derivatives," Interscience Publishers, New York, N. Y., 1943, p. 454. Our results indicate the same trend.

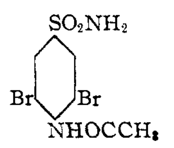
STATE UNIVERSITY OF NEW YORK
COLLEGE OF FORESTRY
SYRACUSE 10, N. Y.

RECEIVED DECEMBER 15, 1950

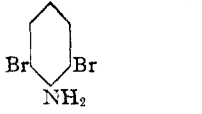
Acetylation of 3,5-Dibromosulfanilamide

BY MARGARET K. SEIKEL AND N. ALICE STRAHAN[1]

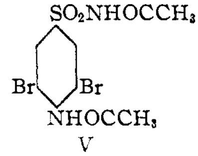
In continuation of the work on halogenated derivatives of sulfanilamide,[2,3,4] the acetyl derivatives of 3,5-dibromosulfanilamide (I) have been prepared. Like the analogous dichloro compound (II),[4] I yields the four possible acetyl derivatives, III, IV,[5] V and VI directly and under practically identical conditions. Increases in the time required for complete acetylation in the preparation of IV, V and VI and a decrease for III represent the only significant differences.



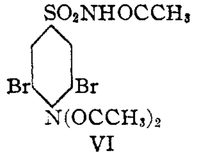
III



IV



V



VI

The properties of III, IV, V and VI are also very

---

[1] Submitted in June, 1950, in partial fulfillment for the degree with honors.

[2] M. K. Seikel, THIS JOURNAL, **62**, 1214 (1940).

[3] M. K. Seikel, *Org. Syntheses*, **24**, 47 (1944).

[4] M. K. Seikel, THIS JOURNAL, **70**, 3344 (1948).

[5] Previously prepared by the bromination of N^1-acetylsulfanilamide, m.p. 193.8–194.6° (uncor.), by E. H. Wells, *J. Assoc. Official Agri. Chem.*, **25**, 747 (1942); *C. A.*, **36**, 6751 (1942).

TABLE I

ANALYSES AND PHYSICAL PROPERTIES

Compound	Formula	Carbon, % Calcd.	Carbon, % Found[a]	Hydrogen, % Calcd.	Hydrogen, % Found[a]	Neut. equiv. Calcd.	Neut. equiv. Found[b]	M.p., °C.	Recrystn.[c] solvents, ml./g.	Recov., %	G./100 ml. cold H_2O	pH satd. H_2O sol.[d]
III	$C_8H_8Br_2N_2O_3S$	25.82	25.89	2.17	2.16			252–253	50% EtOH[e]	70	0.031[f]	
IV	$C_8H_8Br_2N_2O_3S$	25.82	26.11	2.17	2.28	372	372	199–200[g]	50% EtOH[h] 30–50	68–87	.007[i]	4.49
V	$C_{10}H_{10}Br_2N_2O_4S$	29.00	29.17	2.43	2.43	414	413	225–226	70% EtOH[j,k] 9–12	61–79	.062[i]	3.55
									50% acetone 12–50	61–84		
VI	$C_{12}H_{12}Br_2N_2O_5S$	31.60	32.02	2.65	2.71	456	456[l]	198–199	50% acetone[m] 12–35	75–88	.035[i,n]	3.69

[a] Best of two or three checking results. [b] Determined by titration in 95% alcohol with phenolphthalein indicator; best of two or three checking results given. [c] All compounds became colorless, generally without the use of decolorizing carbon. [d] Determined by a Beckman pH meter using a glass electrode. [e] One recrystallization was generally done from glacial acetic acid, 75% recovery, as it purified low melting samples well; 1,4-dioxane purified III well but the recovery was about 50%. [f] Determined by evaporating a saturated solution to dryness. [g] See footnote 5. [h] Decolorizing carbon was necessary. [i] Determined by titrating a saturated solution. [j] 1,4-Dioxane or diluted dioxane was also used; water alone gave very low recoveries. [k] The first material which separated on recrystallization seemed to be impure although it was high melting; it probably contained traces of less soluble III. Second precipitates, melting lower than the crude materials, gave better analytical values. [l] Sapn. equiv., calcd., 228, found, 230.[b] For method see earlier work, footnote 4, p. 3347. [m] With 50% alcohol, 20–25 ml., 60–93% recoveries. [n] This value is the only one higher than those of the dichloro analogs. Such a discrepancy may be caused by slight hydrolysis of the second N[4]-acetyl group.

similar to those of the corresponding derivatives of II.[4] The differences are: (1) except for VI, they are one-half to one-fourth as water-soluble; (2) the melting points of III and V are much higher; (3) V does not appear to form a stable hydrate. Whether IV and I form a complex was not investigated. Preliminary potentiometric titrations indicated that the ionization constants of the three acidic compounds, IV, V and VI were similar to that of benzoic acid.

This work offers a second example[4] of the differential acetylation of the amino and amido groups, by control of the amount of sulfuric acid used as a catalyst or by the use of basic media, which distinguishes the 3,5-dihalogenosulfanilamides from sulfanilamide and its non-diortho substituted derivatives.

Experimental[6]

N⁴-Acetyl-3,5-dibromosulfanilamide (III).—A 0.7-g. sample of I[7] was monoacetylated in the N[4] position exactly as described earlier for II[4]; the reaction, however, was complete after ten minutes. A 71% yield (0.56 g.) of crude, pale pink III, m.p. 240–249°, and an 18% yield (0.16 g.) of light peach-colored V, m.p. 198–212°, were obtained. Before recrystallization III was extracted with a saturated sodium bicarbonate solution; this operation removed further traces of V and raised the melting point to 252–254°. If longer times were allowed for the reaction, the amount of diacetylation increased at the expense of monoacetylation.[8] Substitution of acetyl chloride for acetic anhydride produced no acetylation. III was insoluble in carbonate solution, non-titratable and non-diazotizable.[9]

N¹-Acetyl-3,5-dibromosulfanilamide (IV).—A 2.0-g. sample of I,[7] dissolved in 2.4 ml. of warm pyridine, was monoacetylated in the N[1] position exactly as described for II[4]; it was necessary, however, to heat the reaction mixture for 30 minutes on the steam-bath to complete the reaction. A 93% yield (2.08 g.) of cream-colored product, m.p. 206–218°, was obtained. The use of larger volumes of pyridine or shorter times of reaction lowered the yield. Purification of this material lowered its melting point at first[10] and then raised it slightly. IV was soluble in bicarbonate solution, titratable with 0.1 N alkali and diazotizable.[9]

N¹,N⁴-Diacetyl-3,5-dibromosulfanilamide (V).—I[7] (0.5 g., 0.00151 mole) was diacetylated in a mixture of acetic acid and acetic anhydride containing sulfuric acid in a manner analogous to that described for II[4] except that the amount of anhydride was reduced to 1.24 times the theoretical amount (0.00375 mole, 0.35 ml.). Spontaneous monoacetylation required 8 to 15 minutes at room temperature. The mixture was then boiled for only three or four minutes, during which time the monoacetyl derivative dissolved, but unlike the chloro analog the diacetyl derivative generally did not precipitate until the reaction mixture was cooled. After the usual method of isolation, 0.58 g. (93% yield) of flesh-colored powder was obtained, m.p. 229–231°. Other runs gave lower melting crude products. The amount of acetic acid used was not critical, but low yields resulted if none was used. Longer boiling caused too much decomposition, but no boiling gave a mixture of III and V. Larger amounts required longer times for reaction. V is soluble in bicarbonate solution, titratable with 0.1 N alkali but non-diazotizable. If heated rapidly, some samples appeared to melt below 100° and then resolidify, but no quantitative data indicating a stable hydrated form analogous to that of N¹,N⁴-diacetyldichlorosulfanilamide[4] was obtained.[9]

N¹,N⁴,N⁴-Triacetyl-3,5-dibromosulfanilamide (VI).—A 2.0-g. sample of I[7] was triacetylated with excess acetic anhydride containing 0.0001 ml. of concentrated sulfuric acid per 0.5 ml. of anhydride by the method previously described for II.[4] No visible evidence of monoacetylation occurred when the mixture was shaken at room temperature for 15 minutes. It was necessary to reflux the mixture for one-half hour in order to complete the reaction. The cream-colored product obtained by adding water to the light brown solution weighed 2.38 g. (86% yield) and melted at 195–197°. Halving the time of reaction decreased the yield to 60%. VI was soluble in bicarbonate, gave both neutralization and saponification equivalents[4] with 0.1 N alkali and was non-diazotizable.[9]

DEPARTMENT OF CHEMISTRY
WELLESLEY COLLEGE
WELLESLEY, MASS.

RECEIVED DECEMBER 4, 1950

---

[6] Melting points are uncorrected and were taken by the method described by S. P. Mulliken, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1904, Vol. I, p. 218, on a 360° thermometer immersed in Dow Corning Silicone, DC 550.

[7] M.p. 234–236°, recorded 239–240°.[3,5]

[8] With II this did not occur.

[9] For data on recrystallization, melting point, analyses, solubility in water and pH of aqueous solutions, see Table I.

[10] The N¹-acetyl derivative of II behaved similarly.

Some Substituted Crotonolactones and Oxazolones

BY WALTER T. SMITH, JR., AND CALVIN HANNA

Substituted oxazolones and crotonolactones have been prepared by the condensation of suitable compounds with hippuric acid and β-benzoylpropionic acid. Thus, Erlenmeyer and Arbenz[1] prepared 2-phenyl-4-phthalal-5-oxazolone from phthalic anhydride and hippuric acid, and Borsche[2] prepared α-phthalal-γ-phenylcrotonolactone from

---

[1] E. Erlenmeyer and E. Arbenz, *Ann.*, **337**, 302 (1904).

[2] W. Borsche, *Ber.*, **47**, 2718 (1914).